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GROUND WATER AND ECOSYSTEMS RESTORATION RESEARCH

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Monitored Natural Attenuation of Chlorinated Solvents

Introduction to the Problem

Monitored natural attenuation (MNA) is frequently used as a remedy, or part of the remedy, for ground water contamination from chlorinated solvents at Superfund and Resource Conservation and Recovery Act sites. EPA guidance requires that the processes that cause natural attenuation be understood and documented on a site-specific basis before monitored natural attenuation is accepted as a remedy.

Background

Natural biological degradation through anaerobic reductive dechlorination is the most thoroughly studied process that accounts for natural attenuation of chlorinated solvents. There is less understanding and appreciation of the role of other anaerobic degradation processes, in particular, the contribution of nonbiological transformations carried out by reactive minerals in the aquifer matrix. The abiotic degradation of chlorinated solvents (such as perchloroethylene [PCE] and tetrachloroethylene [TCE] and their degradation products the dichloroethanes [DCEs]) generally proceeds through a pathway that does not produce vinyl chloride. A failure to accumulate vinyl chloride has been taken as an indication that the DCEs are not degraded in contaminated ground water, even though computer modeling indicates that DCE must be removed from the plume to explain the distribution of DCE at field scale.

Objectives

EPA's objective is to develop tools to predict the rate and extent of nonbiological transformations of chlorinated solvents in contaminated ground water that are associated with iron and sulfur minerals, such as mackinawite (FeS), magnetite, and green rusts.

Approach

EPA's approach is to:

- Conduct microcosm studies using core materials from plumes that show apparent removal of chlorinated solvents, such as PCE, TCE, or the DCEs, without accumulation of vinyl chloride
- Conduct analyses for minerals in the aquifer matrix (magnetite, mackinawite, pyrite, green rusts) that have been shown to transform chlorinated solvents or their daughter products
- Associate the presence of the minerals with the rate of removal of the contaminants
- Synthesize the minerals in the laboratory
- Determine the rate of degradation of PCE, TCE, cis-DCE and vinyl chloride on the minerals expressed as a rate normalized to the bulk concentration of the mineral, or the surface area of the mineral presented to the contaminated water

Accomplishments to Date (August 2009)

Microcosm studies have been concluded to compare the rate of degradation of PCE, TCE, and cis-DCE in sediment containing magnetite. The first order rates of degradation are slow (0.3 to 1 per year in material with 0.2 percent to 0.4 percent by weight magnetite), but are useful for MNA in many plumes of contaminated ground water. (Ferrey, et al. 2004)

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A laboratory column study determined the rate of degradation of TCE on biogenic FeS (mackinawite). The rate varied from 0.5 to 2.3 per day per mole of FeS in contact with ground water. (Shen and Wilson 2007) Over time the biogenic FeS transformed to pyrite. (He, et al. 2008) The concentration of FeS in aquifer sediment can conveniently be estimated from the acid volatile sulfide (AVS) in the sample. A concentration of 100 milligrams per kilogram AVS should produce a first order rate of degradation of TCE of 10 per year. Laboratory studies with synthetic mackinawite produced a rate from 0.4 to 0.8 per day per mole of FeS in contact with ground water. The surface area specific rate constant was $5 \times 10^{-5} \text{ L m}^{-1} \text{ day}^{-1}$.

Near-Future Tasks

An EPA report is in preparation: *Identification and Characterization Methods for Reactive Minerals Responsible for Natural Attenuation of Chlorinated Organic Compounds in Ground Water*. It should be available by March 2010.

Experiments with synthetic pyrite will begin in late 2009.

References

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